ECO-FRIENDLY GREEN SYNTHESIS OF COPPER NANOPARTICLES ASSISTED BY ERYTHRINA VARIEGATE LEAVES EXTRACT

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ABSTRACT

The development of nanotechnology towards synthesis of nanoparticles for the bio application widely finds its importance among the researchers. Ecofriendly green syntheses of copper nanoparticles were carried out using Erythrina variegate leaves extract. The formation of the copper nanoparticles was first identified by comparing the color of the extract and its assisted copper nanoparticles medium. The copper nanoparticles were characterized by UV, FT-IR, XRD and FESEM analysis. UV-Visible absorbance of copper nanoparticles was observed at 560nm. FT-IR stretching frequencies at 408.3 cm-1 and at 418.5 cm -1 proved that these nanoparticles were bonded to the oxygen present in the bio-active constituents of Erythrina variegate and indicated the formation of Metal-oxygen bonds at these frequencies. XRD & FESEM analysis of copper nanoparticles proved that they exist in spherical; face centered cubic (fcc) crystalline structure with size of 29 nm approximately.

Keywords: Erythrina variegate, copper nanoparticles, FT-IR and FESEM.

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Introduction

Nanotechnology plays a very important role in modern research[1,2] in the treatments of infection [3], cancer [4] , allergy [5] , diabetes [6] and inflammation[7] . Green chemistry is used to minimize the use of hazardous to environment [8-10]. Many researchers used green synthesis methods for different metal nanoparticles due to their growing need of eco-friendly properties [11, 12]. In this method, the plant extract has been used as capping and reducing agent for the synthesis of copper nanoparticles due to their reducing properties present in the leaves extract [13, 14]. Copper is most widely used material in the world due to its varied properties compared to other metals in a cost effective manner [15,16]. Copper nanoparticles act as antimicrobial agent in various fields [17-19]. Studies on phytochemical analysis of Erythrina variegate species have demonstrated that alkaloids and flavonoids were found to be major constituents [20]. Alkaloid fraction from the bark showed several characteristic pharmacological effects such as neuromuscular blocking, CNS depressant and anticonvulsant effects. The leaves are used to stimulate lactation and menstruation. It is commonly mixed with castor oil to treat dysentery. The bark is used as a laxative, diuretic, and expectorant.[21,22]. Different parts of E.Variegata have used in traditional medicine as nervine sedative, febrifuge and anti-asthmatic. Crude extract obtained from the E. variegate have potential effects for the treatment of some diseases like convulsion, fever, inflammation, bacterial infection, insomnia, helminthiasis, cough, cuts and wounds [23-27].

Knowing the importance of Erythrina variegate leaves extract constituents and copper nano particles biological importance, and in continuation of our work on bioactivity and stability prediction of phytoconstituents present in Erythrina variegate [28-30], we planned to synthesize

copper nano particles by greener method using Erythrina variegate leaves extract in an ecofriendly manner.

Experimental Method

a) Materials

The leaves of Erythrina variegate were collected from Sivakasi areas of virudhunagar district, Tamilnadu. Copper sulphate of Merck grade was used

b) Methods

i. Preparation of Aqueous Extract of Erythrina variegate leaves extract

About 5 gram of the powdered sample of Erythrina variegate leaves were weighed and dissolved in 100ml of distilled water in a round bottomed flask. The soxhlet apparatus was set up and the reaction was carried out until a clear solution was obtained. The extract was filtered by Whatmann No1 filter Paper. Then the filtrate was stored in an air tight seal pack under -4° C for nanoparticle synthesis.

ii. Synthesis of Copper Nanoparticles from Erythrina Variegate Leaves Extract

About 10 ml of the aqueous Erythrina variegate leaves was added into of 40 ml aqueous solution of 1 mM copper sulphate in a conical flask for reduction into Cu^{+} ions and kept for incubation (darkroom) at room temperature. Here the extract acts as reducing and stabilizing agent for 1mM of $CuSO_4$. Reduction of copper sulphate to copper ions was confirmed by the color changes of the extract from light yellow to dark brown as given in the **Figure -1**. The formation of copper nanoparticles was also confirmed by spectrophotometric identification. The formation of copper nanoparticles was also confirmed by spectrophotometric identification.

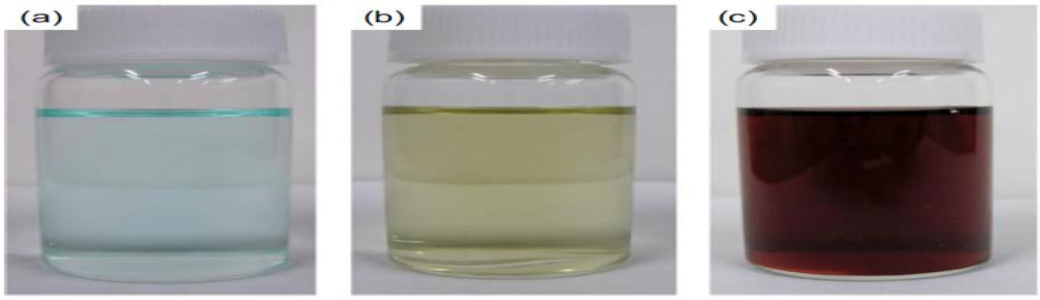

Figure - 1

(a) $CuSO_4$solution (b) Erythrina variegate aqueous extract

(c) Erythrina variegate + $CuSO_4$solution

iii. Separation of Copper Nano particles:

The synthesized copper nano particles were separated by means of centrifugation (spectrofuge 7M) at 10,000 rpm for 30 mins.

iv. Characterization of Copper Nanoparticles

Characterisation of copper nano particles was first carried out using UV-Visible absorption spectrophotometer 2400PC with a resolution of 1nm between 300 and 900nm possessing a scanning speed of 300nm/min. The characterization of functional groups on the surface of copper nanoparticles by leaves extract were investigated by FT-IR spectra analysis using (Shimadzu FT-IR 8400S model) and the spectra was scanned in the range of 4000-400cm^{-1} range at a resolution of 4 cm^{-1} . The particle size and nature of the copper nano particles were determined using XRD PW 3050/60 X-pert PRO operating at a voltage of 45 KV, a current of 40mA with Cu K alpha radiation at 2θ angle ranging from 5° to 90°. A thin film of copper nanoparticles was made by dipping a glass plate in a solution and carried out for X-ray diffraction studies. FESEM analysis was done by using a JSM6701F – 6701 model.

Results and Discussion

The formation of copper nanoparticles can be observed by the change in the color of the solution from light yellow color to dark brown color after six hours of incubation as given as in the **Figure – 1**.

i)**UV-Visible Spectral Analysis**

Figure – 2 showed that the UV absorption spectra of the copper nanoparticles appeared at 560 nm and this result was similar with Curtis et al results for the copper nanoparticles within the range of 560- 640 nm. The peak value was found to be gradually decreased with increase in particle size. Copper Surface Plasmon Resonance effects decrease with the time because of the oxidation of the synthesized copper nanoparticles

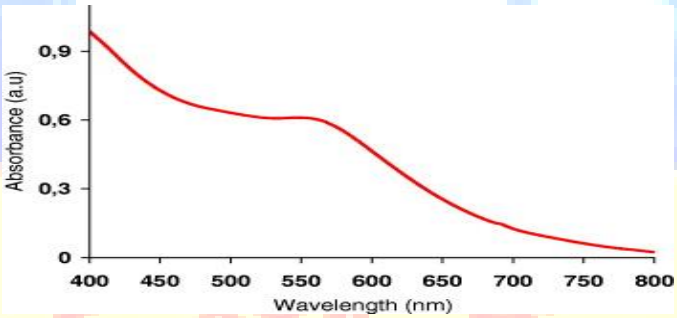

Figure - 2 UV-Visible spectra of copper nano particles.

i) Fourier Transform-Infrared Spectral Analysis

The FTIR analysis was used to identify the capping, reducing and stabilizing capacity of the leaves extract. **Figure - 3**, aqueous extract of the leaves showed the broad band between 3200 cm $^{-1}$ - 3600 cm $^{-1}$ indicated the presence of bonded –OH groups. The band at 1641 cm^{-1} indicated the presence of carbonyl group. The copper nanoparticles formed

using Erythrina variegate(**Figure - 4**)showed the IR stretching frequency at 408.3 cm $^{-1}$(for metal – oxygen binding). The diminished –OH stretching frequency in the region of 3200 cm $^{-1}$ to 3600 cm $^{-1}$ and the diminished carbonyl stretching frequency at 1641 cm^{-1} for the Erythrina variegate leaves extract compared to copper nanoparticles showed that the copper nano particles were formed by binding with the –OH oxygen and carbonyl oxygen of bio-active compounds present in Erythrina variegate .The other peaks obtained in copper nanoparticle are 3761, 3846, 3977 cm^{-1} due to O-H Stretching of hydrogen bonded alcohols and phenols .The FTIR analysis of copper nano particles suggested that they might be bonded to the organic molecules such as polyphenols, alkaloids and terpenoids and flavonoids etc.,. The chemical constituents present in plant leaves extract such as Flavonoids, alkaloids and fatty acids are responsible for the reduction of copper ions to copper nanoparticles due to their capping and reducing capacity.

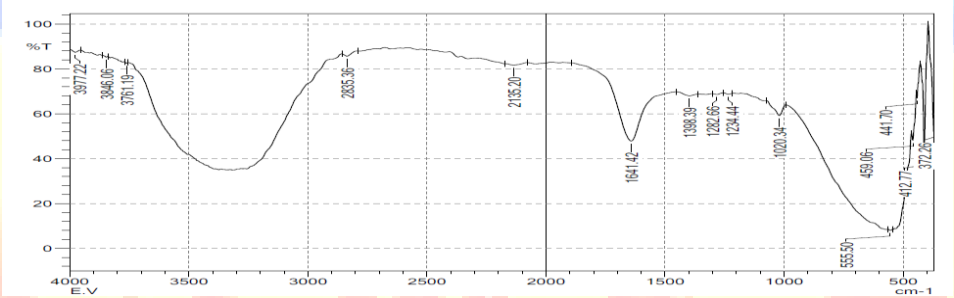

Figure – 3 FT-IR Spectrum of the Erythrina Variegate leaves Extract.

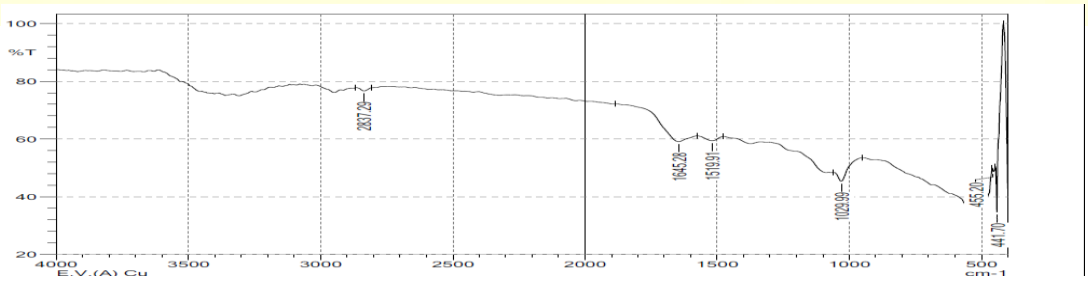

Figure – 4 FT-IR Spectrum of The copper nanoparticles

X-Ray Diffraction Spectroscopy

XRD pattern of synthesized Copper nanoparticles using a leaf extract of Erythrina variegate was shown in **Figure 5**. The XRD pattern shows a high crystallinity of Copper sample level with diffraction angles of 22.3°, 25.9°, 28.3° and 44.8°, which correspond to the characteristic face centered cubic (FCC) of copper lines indexed at (111), (200), (210) and (222), respectively. The diffraction angle was observed at 21.1° .The size of the Nanoparticles obtained were estimated to be 77 nm using Debye-Scherrer Equation, which may indicate a high surface area, and surface area to volume ratio of the nano-crystals.

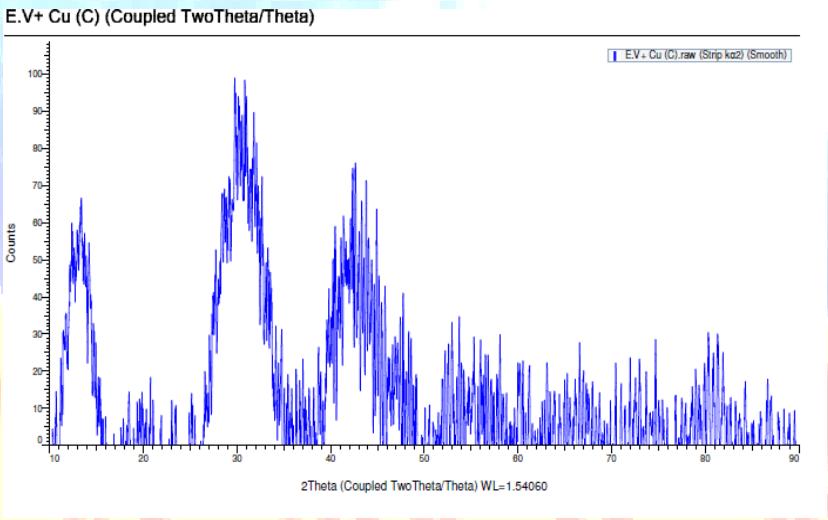

Figure –5 XRD Spectrum of copper nanoparticles

Field Emission Scanning Electron Microscopy Analysis

Field Emission scanning electron microscopy analysis was carried out to understand the topology and the size of the copper nanoparticles. The electrostatic interactions and hydrogen bond between the bio-organic capping molecular bonds were responsible for the synthesis of copper nanoparticles using plant extract. The result showed that the synthesised copper nanoparticles were in polydispersed spherical in shape and in the

particles sizes range between 26-52nm with average size of 32 nm as given in the **Figure -6**. FESEM image proved the formation of copper nanoparticles in an ecofriendly greener way.

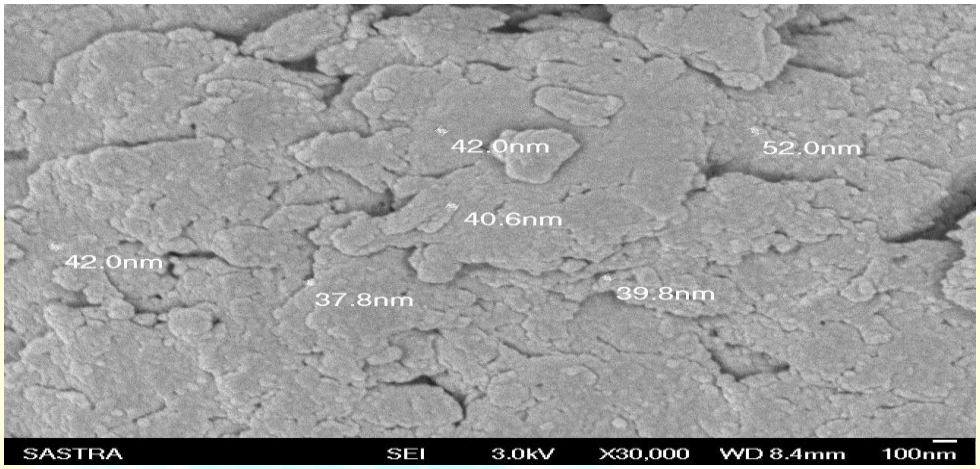

Figure – 6 FESEM analyses of copper nanoparticles

Conclusion

Green synthesis of copper nanoparticles was carried out using Erythrina variegate leaves extract and the formation of copper nano particles were confirmed as per as the followings:

- Formations of copper nanoparticle was first confirmed by colour changes from light yellow to dark brown of Erythrina variegate leaves extract.
- UV absorption of copper nanoparticle showed the characteristic absorbance at 560 nm.
- FT-IR studies of copper nanoparticles showed that the IR stretching frequency at 408.3 cm^{-1}(for copper – oxygen binding). This was confirmed by comparing FT-IR spectrums of Erythrina variegate leaves extract and their assisted copper nanoparticles.
- The formation of copper nanoparticles was also proved by XRD studies which showed the characteristic face centered cubic (FCC) of copper lines indexed at (111), (200), (210) and (222) planes respectively.
- Field emission Scanning Electron Microscopy (FESEM) studies also confirmed the formation of copper nanoparticles as their sizes ranges from 26 – 52 nm

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